



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF:

OKINAKA ET AL.

SERIAL NO. 09/994,903

GROUP ART UNIT: 1745

FILED: November 28, 2001

EXAMINER: R. ALEJANDRO

FOR: CATHODE ACTIVE MATERIAL  
FOR NON-AQUEOUS ELECTROLYTE  
SECONDARY CELL AND PROCESS  
FOR PRODUCING THE SAME

DECLARATION UNDER 37 C.F.R. 1.132

HONORABLE COMMISSIONER OF PATENTS & TRADEMARKS

WASHINGTON, D.C. 20231

SIR:

Now comes Hideaki MAEDA, a citizen of Japan, and a resident of 404-1-9-2, Akasaki, Onoda-shi, Yamaguchi-ken, Japan, who declares and says that:

1. I graduated from the Department of Applied Chemistry, Faculty of Science, Konan University in March, 2000.

2. I am currently employed by TODA KOGYO CORPORATION since April, 2000.

3. I am familiar with the work related to U.S. Patent Application, Serial No. 09/994,903, and am a co-inventor of U.S. Patent Publication No. US-2003-0049534-A1.

4. Under my control and supervision the following experiments were conducted:

Experiment 1 (Examples 2 of Japanese Patent Publication  
(KOKAI) 11-67209)

Commercially available lithium hydroxide, cobalt carbonate and manganese oxide were mixed at a Li:Co:Mn:Mg atomic ratio of 1.0:0.9:0.1 in a mortar. The resulting mixture was sintered at a temperature of 750°C for 20 hours in dry air, thereby obtaining an oxide composite having a composition of  $\text{LiCo}_{0.9}\text{Mn}_{0.1}\text{O}_2$ .

The obtained oxide composite was pulverized by a jet mill to obtained oxide composite particles having a median diameter of around 0.1  $\mu\text{m}$ .

Experiment 2 (Examples 28 of European Patent No. 1 154 503)

Commercially available lithium carbonate, cobalt oxide, manganese oxide and magnesium carbonate were mixed at a Li:Co:Mn:Mg molar ratio of 1.02:0.98:0.01:0.01. The resulting mixture was charged into an alumina crucible and sintered in a dry atmosphere.

However, there is no description of the sintering condition in European Patent No. 1 154 503. So, in order to determine the sintering condition in the production of a positive electrode active material, documents which were published prior to the filing date of European Patent No. 1 154 503 and in which the applicant (Sony Corporation) is the same as European Patent No. 1 154 503, were further searched. As a result, it has been found out that Japanese Patent Publication (KOKAI) 2001-23614 published on January 26, 2001, discloses that as a positive electrode active material,

lithium carbonate of 1.0 mole was mixed with manganese oxide of 2.0 mole, and the obtained mixture was sintered at a temperature of 800°C for 15 hours in air.

So, the above-mentioned sintering treatment into the alumina crucible was conducted at a temperature of 800°C for 15 hours in air, thereby obtaining powders having a composition of  $\text{LiCo}_{0.98}\text{Mn}_{0.01}\text{Mg}_{0.01}\text{O}_2$ .

Experiment 3 (Examples 2 of Japanese Patent Publication  
(KOKAI) 4-237968)

As a positive electrode active material,  $\text{LiCo}_{0.9}\text{Mn}_{0.1}\text{O}_2$  is disclosed in the Example 2. However, there is no description of the production method of the positive electrode active material in Japanese Patent Publication (KOKAI) 4-237968.

So, in order to determine the production method of the positive electrode active material, documents which were published prior to the filing date of Japanese Patent Publication (KOKAI) 4-237968 and in which the applicant (Matsushita Electric Industrial Co., Ltd.) is the same as Japanese Patent Publication (KOKAI) 4-237968, were further searched. As a result, it has been found out that Japanese Patent Publication (KOKAI) 3-201368 published on September 3, 1991, discloses that commercially available lithium carbonate, cobalt carbonate, oxide of W, Mn, Ta, Ti or Nb as M oxide were mixed at a Li:Co:M molar ratio of x:1-y:y. The resulting mixture was sintered at a temperature of 800°C for 15 hours in air.

Accordingly, the positive electrode active material:  $\text{LiCo}_{0.9}\text{Mn}_{0.1}\text{O}_2$  which is disclosed in the Example 2 was produced as follows.

Commercially available lithium carbonate, cobalt carbonate, manganese oxide were mixed at a Li:Co:Mn molar ratio of 1.0:0.9:0.1. The resulting mixture was sintered at a temperature of 800°C for 15 hours in air, thereby obtaining a positive electrode active material having a composition of  $\text{LiCo}_{0.9}\text{Mn}_{0.1}\text{O}_2$ .

Various properties of the obtained products were measured by the following methods.

(1) The cathode active material was measured and identified using a Powder X-ray Diffraction Analyzer manufactured by Rigaku Denki Kogyo Co., Ltd. (Cu-K $\alpha$ ; 40 kV; 40 mA). Also, the lattice constant of the active material was calculated from respective diffraction peaks of the powder X-ray diffraction curve obtained above.

(2) The crystallite size of the cathode active material was calculated from the respective diffraction peaks of the powder X-ray diffraction curve obtained above.

(3) The elemental analysis was conducted using an inductively coupled high-frequency plasma atomic emission spectroscope "SPS-4000 Model" manufactured by Seiko Denshi Kogyo Co., Ltd.

(4) The cell characteristics of the cathode active material were evaluated by a coin-shaped cell constituted from

a cathode, an anode and an electrolyte solution prepared by the following methods.

<Preparation of cathode>

The cathode active material, acetylene black as a conductive agent, and polyvinylidene fluoride as a binder were accurately weighed at a weight ratio of 85:10:5, and intimately mixed with each other in a mortar. The resultant mixture was dispersed in N-methyl-2-pyrrolidone to prepare a cathode slurry. Then, the obtained slurry was applied onto an aluminum foil as a current collector to form a coating film having a thickness of 150  $\mu\text{m}$ , vacuum-dried at 150°C, and then punched into a disc shape having a diameter of 16 mm, thereby producing a cathode.

<Preparation of anode>

A metallic lithium foil was punched into a disc shape having a diameter of 16 mm, thereby producing an anode.

<Preparation of electrolyte solution>

Lithium phosphate hexafluoride ( $\text{LiPF}_6$ ) as an electrolyte was added in an amount of 1 mol/liter into a mixed solution containing ethylene carbonate and diethyl carbonate at a volume ratio of 50:50, thereby preparing an electrolyte solution.

<Assembling of coin-shaped cell>

In a globe box maintained under an argon atmosphere, the above positive and anodes were fitted via a polypropylene

separator in a casing made of SUS316 stainless steel. Further, the electrolyte solution was filled in the casing, thereby producing a CR2032-type coin-shaped cell.

<Evaluation of cell>

The above-produced coin-shaped cell was subjected to a charge/discharge cycle test for secondary cells. The charge and discharge cycles were repeated at a temperature of 60°C and a cathode current density of 0.2 mA/cm<sup>2</sup> while varying the cut-off voltage from 3.0 to 4.25 V.

Table

Examples and Comparative Examples	Properties of cathode active material			
	Mn content (x)	Mg content (y)	Lattice constant (Å)	
			a-axis	c-axis
Our invention	0.008-0.18	0-0.18	2.81-2.83	14.080-14.160
Experiment 1	0.1	0	2.817	14.078
Experiment 2	0.01	0.01	2.817	14.069
Experiment 3	0.1	0	2.817	14.078

Table (continued)

Examples and Comparative Examples	Properties of cathode active material		
	Particle size ( $\mu\text{m}$ )	BET specific surface area ( $\text{m}^2/\text{g}$ )	Crystallite size ( $\text{\AA}$ )
Our invention	0.1-5.0	0.1-2.5	400-1200
Experiment 1	0.1	1.2	483
Experiment 2	2.0	0.4	755
Experiment 3	0.1	1.2	483

Table (continued)

Examples and Comparative Examples	Properties of secondary cell	
	Initial discharge capacity ( $\text{mAh/g}$ )	Capacity retention percentage after 50 cycles ( $\%/50\text{cy.}$ )
Our invention	135-160	90-99
Experiment 1	142	78
Experiment 2	146	81
Experiment 3	141	77

Remarks

As seen from the above, the oxide composite particles obtained in Experiment 1 (Examples 2 of Japanese Patent Publication (KOKAI) 11-67209) has a c-axis length of lattice constant of  $14.078 \text{ \AA}$ , the powders obtained in Experiment 2

(Examples 28 of European Patent No. 1 154 503) has a c-axis length of lattice constant of 14.069 Å, and the positive electrode active material obtained in Experiment 3 (Examples 2 of Japanese Patent Publication (KOKAI) 4-237968) has a c-axis length of lattice constant of 14.078 Å, which are out of the range of our invention.

As a result, the capacity retention percentages after 50 cycles at 60°C of the secondary cells produced using such a cathode active materials are inferior to that of our invention.

6. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: 20. January 2004

Hideaki Maeda  
Hideaki MAEDA